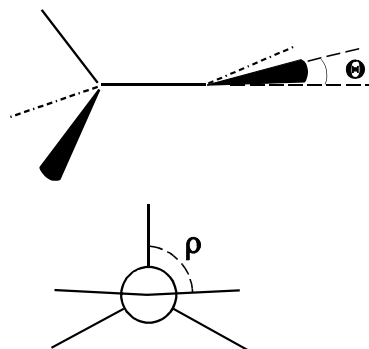


# Infrared Spectrum and Internal Dynamics of the Ethyl Radical

The ethyl radical ( $C_2H_5$ ) is the simplest alkyl radical that exhibits the torsional and low-frequency skeletal vibrational motions which are expected to dominate the internal dynamics of all heavier members of this radical class. Despite its importance, few spectroscopic studies have been carried out. The lowest accessible electronic excited states tend to predissociate and lie in the ultraviolet. Infrared spectroscopy does not suffer from these disadvantages, but has traditionally lacked the sensitivity to allow us to access gas-phase spectra of such complex and chemically reactive species. Ethyl possesses two low-frequency vibrational modes: a torsion, or internal rotation, and an out-of-plane rocking of the  $-CH_2$  part of the molecule at the radical center. These modes are illustrated schematically in figure 1. The nuclear motions corresponding to these vibrational modes



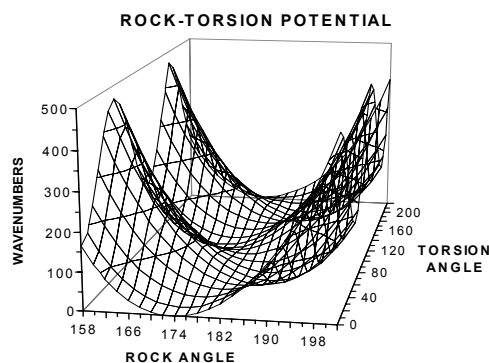
**Figure 1:** Schematic representation of the internal rotation ( $\rho$ ) and  $CH_2$  rocking ( $\theta$ ) vibrational modes in ethyl

are found by from the solution of the Schrödinger equation and are governed by the radical's potential energy surface.

Figure 2 illustrates the shape of this potential surface along cuts through the full, multidimensional, potential energy surface corresponding to the low frequency vibrational modes of interest. The minimum along the rocking angle axis corresponds to an angle of close to  $180^\circ$  while those on the torsion angle axis correspond to the multiple equivalent minima as one end of the radical rotates relative to the other. The positions of the minima obviously depend on the  $CH_2$  rocking coordinate, i.e. if it is greater or less than  $180^\circ$ , reflecting the degree of coupling between these modes.

Experimental studies of the vibration-rotation spectrum of the radical can give information on the size of the barriers in the potential shown in figure 2 as well as more traditional quantities such as the rotational constants and the vibrational frequencies. Due to the chemical

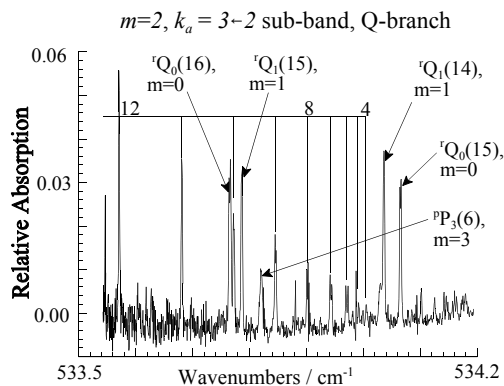
importance of this radical, we have made extensive measurements of its infrared spectrum using transient diode laser absorption spectroscopy to detect the  $CH_2$  rocking vibrational fundamental near  $500\text{ cm}^{-1}$ . The spectrum contains many torsion-rotational sub-bands that



**Figure 2:** Calculated electronic energy of ethyl radical as a function of both the torsional angle and the rocking angle of the  $CH_2$  group.

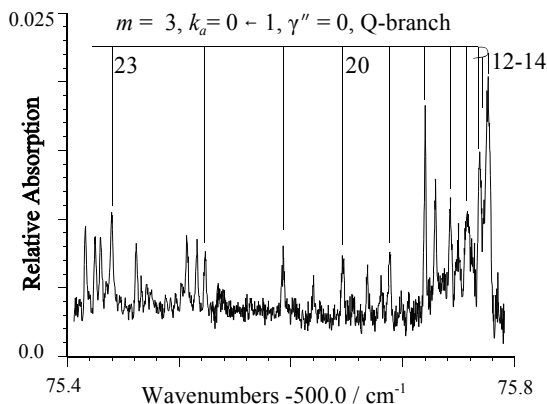
cause it to be very complicated. For example, figure 3 shows a short section of the spectrum and indicates rotational and torsional quantum number assignments for the stronger lines.

More than 450 individual torsion-rotational lines belonging to the  $CH_2$  rocking fundamental mode have now been assigned. Their frequencies contain information on the structure and torsional potential surface in the radical. For example, some torsional levels with torsional quantum number,  $m$ , = 3 are directly affected by the size of the torsional barrier, that is the energy between the minima and maxima on the torsional axis of figure 2. Observation of transitions in the infrared



**Figure 3:** Low-J part of the  $m=2$ ,  $k_a=3-2$  sub-band Q-branch with higher-J members of other sub-branches labeled.

spectrum that belong to such levels can be used to determine the size of the barrier. An example is shown in figure 4. These and many other spectra were used to determine parameters appearing in the effective Hamiltonian describing the ground and CH<sub>2</sub>-rock excited



**Figure 4** The low frequency,  $\gamma = 1-0$ , component of the  $m=3$ ,  $k_a = 0-1$  sub-band. The Q-branch forms a head at intermediate  $J$ -values then extends to the red. The position of this sub-band is primarily determined by the size of the torsional barrier,  $V_6'$ , in the upper vibrational level.

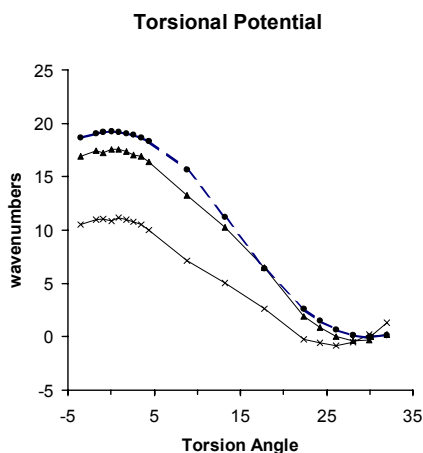
vibrational levels of the radical. In particular, the barrier to internal rotation was found to decrease from 16.62 cm<sup>-1</sup> in the ground, zero point, vibrational level to 10.29 cm<sup>-1</sup> when one quantum of CH<sub>2</sub> rock vibration was excited.

These experimental quantities can be directly compared to what are calculated using modern quantum

chemistry packages. While figure 2 shows the electronic contribution to the potential surface, comparison with experiment requires an accurate assessment of the effects of nuclear vibrational motions on the effective torsional barrier. In effect, the size of the barrier will depend on the expectation values of all the other vibrational modes in the molecule. Fortunately, these quantities can also be calculated, and figure 5 illustrates the results for ethyl in the two levels involved in the observed vibrational spectra. These curves are cuts through the full potential energy surface along the torsion coordinate. The irregularities arise because one dihedral angle between hydrogens on each end of the molecule was held fixed to obtain the intermediate points between the minimum and saddle point for the zero point and vibrationally excited levels. There is not a perfect separability between the torsion and other vibrational modes resulting in small irregular variations in the calculated functions. The reliable values at the minimum and saddle point serve to determine the barriers. The almost sinusoidal nature of the curves illustrate the internal rotation is almost, but not quite, a separable coordinate. The effective barriers are found to be 17.6 cm<sup>-1</sup> in the ground state and 10.9 cm<sup>-1</sup> in the excited rocking vibration, in remarkable agreement with experiment. Importantly, the same numerical model can be applied to still heavier alkyl radicals where experimental studies are beyond our present capabilities.

References to published work:

- <sup>1</sup>T. J. Sears, P. M. Johnson, P. Jin and S. Oatis, J. Chem. Phys. **104**, 781 (1996).
- <sup>2</sup>T. J. Sears, P. M. Johnson and J. BeeBe-Wang, J. Chem. Phys. **111**, 9213 (1999).
- <sup>3</sup>P. M. Johnson and T. J. Sears, J. Chem. Phys. **111**, 9222 (1999).



**Figure 5:** Torsional potential for ethyl radical, including vibrational corrections ( $\blacktriangle$  = zero point level,  $\times$  = one quantum of excitation in the CH<sub>2</sub> rocking vibration), for the fully relaxed molecule. The dashed curve is the purely electronic contribution to the potential. The torsional angle is the average angular position of the CH<sub>3</sub> hydrogens, measured by reference to one of them. It is defined with respect to a plane through the C-C bond which is parallel to a line between the CH<sub>2</sub> hydrogens.